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(54) Title: PROCESS FOR MAKING MVTR RESIN

(57) Abstract: The present invention is directed to producing a resin which, when formed into a film, has excellent gas barrier and/or moisture barrier (low MVTR) properties. Further, the resin has a relatively high molecular weight distribution, preferably above 6, and has excellent processability/extrudability. The resin is produced using a cyclopentadienyl chromium compound, preferably a mono CpCr compound, on a support, preferably a silica support. A particularly preferred catalyst for use in the present invention comprises pentamethylcyclopentadienyldimethylchromiumpyridine. Preferably, the catalyst is used in a slurry polymerization process.

1   **PROCESS FOR MAKING MVTR RESIN**

2   FIELD OF THE INVENTION

3   The present invention relates to a process for producing ethylene polymers
4   having excellent resistance to moisture vapor transmission when the resin is
5   formed into a film. Further, the process of the present invention produces
6   MVTR resins which have ease of processing into a film packaging product.

7   The process of the present invention preferably uses a catalyst comprising a
8   cyclopentadienyl chromium compound supported on a solid refractory
9   material, in slurry or gas phase reaction conditions.

10   BACKGROUND OF THE INVENTION

11   Polymeric composition for uses such as food packaging and other
12   applications where good barrier properties against moisture ingress have
13   been known for many years. Use of HDPE (high density polyethylene) for this
14   purpose is disclosed in Kirk-Othmer, 3rd Edition, page 489. However, many
15   HDPE polymers are not readily processable, such as by extrusion, to form
16   packaging products.

17   It is desirable to have an HDPE that has excellent moisture vapor
18   transmission resistance (MVTR) and also is relatively easy to process into a
19   packaging product, such as a film.

20   The general theory of permeation of a gas or liquid through a polymer film is
21   that the permeation rate is the product of a diffusion term and a solubility
22   constant of the gas-liquid in the polymer, each of which is often independent
23   of the other. The process of permeation through a polymeric barrier involves
24   four steps: absorption of the permeating species into the polymer wall;

1   solubility in the polymer wall; diffusion through the wall along a concentration

2   gradient; and desorption from the outer wall.

3   There are certain molecular structures that lead to good barrier properties in

4   polymers. A practical problem, however, is that the property that might result

5   in a good gas barrier very often also results in a poor water barrier. Polarity is

6   a case in point. Highly polar polymers such as those containing many

7   hydroxyl groups [poly(vinyl alcohol) or cellophane] are excellent gas barriers

8   but also are among the poorest water barriers. In addition, they become poor

9   gas barriers when plasticized by water. Conversely, very non-polar

10   hydrocarbon polymers such as polyethylene have excellent water barrier

11   properties and poor gas barrier properties. It is generally thought that in order

12   to be a truly good barrier polymer, the material must have: some degree of

13   polarity such as contributed by a nitrile, ester, chlorine, fluorine, or acrylic

14   functional groups; high chain stiffness; inertness; close chain-to-chain packing

15   by symmetry, order, crystallinity, or orientation; some bonding or attraction

16   between chains; high glass transition temperature (T_g).

17   In some prior instances, co-extruded film including a polyolefin layer and polar

18   resin layer such as EVOH have been modified to improve water barrier

19   properties by including other substances, such as a wax. Thus, according to

20   U.S. Patent 5,141,801, the barrier properties of a co-extruded film having a

21   crystalline polyolefin surface layer can be improved substantially by

22   incorporating a wax into the polyolefin. The film has an interior polymer layer

23   that prevents migration of the wax to the other surface of the film so that wax

24   does not interfere with the printability or heat sealability of the other surface.

25   The wax-containing polyolefin layer also protects the interior layer from

26   adverse effects of moisture, such as when the interior layer comprises EVOH.

27   An interior layer of EVOH may be sandwiched between wax-containing

28   polyolefin layers to fully protect it from moisture.

1   Major processes for producing PE resins, including HDPE, include solution

2   polymerization, slurry polymerization and gas phase polymerization.

3   Catalysts for these processes include Ziegler-Natta catalysts, Cr catalyst

4   (either in homogeneous form or on a solid support), and, more recently,

5   homogeneous or supported metallocene catalysts. The metallocene catalysts

6   can be either mono or bis cyclopentadienyl (Cp) ligands on a transition metal,

7   such as Ti, Zr, Hf, Cr, etc. The Cp ligands in turn can be substituted by

8   various groups.

9   CpCr catalysts are disclosed in U.S. Patents 5,240,895; 5,302,674;

10   5,320,996; 5,393,720; 5,399,634; 5,418,200; and 5,593,931.

11   U.S. Patent 5,418,200, for example, discloses ethylene polymerization using

12   various CpCr +3 valence compounds on a refractory support, such as silica.

13   The '200 patent states that the polymers produced have a polydispersity or

14   molecular weight distribution (MWD) greater than 10, and that the polymers

15   have improved ease of processing, better melt behavior, and other desirable

16   properties such as impact resistance and environmental stress crack

17   resistance. Also, the '200 patent points out that large blow molded products

18   are superior when made with high MWD polymers, and that film is more

19   puncture resistant when made from polymer with a high MWD.

20   The '200 patent does not disclose MVTR properties for film made from the

21   polymers produced per the '200 process.

22   WO 96/19527 (PCT/US95/16570) discloses polyethylene films of

23   advantageous (low) MVTR, wherein the polyethylene resin used to make the

24   film is produced using a metallocene catalyst. The metallocene catalysts are

25   not specifically described in WO 96/19527, but reference is made to

26   co-pending application U.S. Serial No. 08/093,501 for disclosure of the

27   metallocene catalysts useful in the '527 patent application.

1   According to the '527 patent application, the polyethylene resin has a density

2   in the range of from about 0.935 to about 0.965 g/cm^3, a M_w/M_n less than

3   about 3, and an article made using the resin has a water vapor transmission

4   rate less than 0.54 g•mil/100 in^2/day (0.183 g/mm/m^2/day), preferably less

5   than 0.4 g•mil/100 m^2 day (0.135 g/mm/m^2/day).

6   Thus, the films made from the polyethylene according to the '527 patent

7   application have a MWD or polydispersity below 3.

8   U.S. Patent 5,183,792 is directed to producing polyolefin resin using a catalyst

9   comprising chromium and titanium supported on silica. The polymer

10   produced has a high melt index and a narrow molecular weight distribution

11   (MWD). The narrow MWD is indicated in U.S. Patent 5,183,792 as helpful in

12   achieving a low MVTR. As stated in the '792 patent at column 4, lines 35-40:

13   "The product will have a high melt index (MI) and a low high load melt

14   index/melt index ratio (HLMI/MI) and, as is observed when these two

15   properties are high and low respectively, a low water vapor transmission."

16   Also, in *Plastics Technology*, August 1999, in an article by J. Krohn et al. titled

17   "Keep It Dry, Optimize Moisture Barrier in PE Films", at pages 60-61, the

18   authors state "Thus, structure 3 excelled in barrier because it was the only

19   one to have a skin layer of higher MI resin with narrower MWD, both of which

20   contribute inherently to better barrier."

21   <u>SUMMARY OF THE INVENTION</u>

22   According to the present invention, a process is provided for making an

23   ethylene homopolymer having a polydispersity above 4, and wherein the

24   homopolymer is suitable for producing a film having a high barrier to

25   transmission of water or gas, or both, which process comprises contacting

26   ethylene with a catalyst comprising a cyclopentadienyl chromium hydrocarbyl

1　compound on a solid support, under slurry or gas phase polymerization

2　conditions.

3　The process of the present invention is especially advantageous in producing

4　resins which have an MVTR less than 0.4, preferably less than 0.3, still more

5　preferably below 0.25 grams of water per 100 square inches of film per day,

6　for a 1 mil (one thousandth of an inch) thick film.

7　Preferably, the resins produced in accordance with the present invention have

8　a polydispersity or MWD above 4, more preferably between 4.5 and 12, and

9　most preferably between 4.7 and 7.5.

10　Preferred catalysts for use in the process of the present invention are mono or

11　bis cyclopentadienyl chromium compounds, more preferably a mono

12　cyclopentadienyl, on a solid support. Preferably, mono cyclopentadienyl

13　contains one or more substituents. Preferred substituents are hydrocarbyl

14　groups; particularly preferred is cyclopentadienyl substituted with five methyl

15　groups. Preferably the solid support is silica. An especially preferred catalyst

16　for use in the process of the present invention is pentamethyl $CpCr(CH_3)_2Pyr$

17　on a solid support, where Cp represents cyclopentadienyl, and Pyr represents

18　pyridine. Preferred co-catalysts are alumoxanes, especially isobutyl

19　alumoxane (IBAO). Preferred catalysts for use in the present invention are

20　described in more detail below.

21　We have found that use of catalysts such as the aforementioned especially

22　preferred catalyst, under process conditions as described herein, produces

23　substantially linear polyethylene of density at least 0.955 g/cc, with nearly all

24　of the terminal groups of the polyethylene polymer saturated. Preferably, the

25　process conditions are selected to allow the catalyst to react under

26　mechanisms that produce predominately saturated end groups, that is, the

27　methyl end group to olefin end group ratio relatively high, at least 10, and

1   preferably greater than 15, as measured by FTIR (Fortier Transform Infrared

2   spectroscopy).

3   Preferred process conditions, particularly when using the aforementioned

4   especially preferred catalyst, include polymerization reaction zone

5   temperature between 50°C to 100°C, more preferably 70°C to 90°C, with a

6   slurry ethylene concentration of 8-15 weight percent. Hydrogen is a preferred

7   chain transfer agent.

8   Other particularly preferred process conditions are related to the extrusion

9   and pelletization process, and the film process.

10   Ideal compound conditions, or pelletization process are those that do not alter

11   the chemical structure of the polymer; preferably cross-linking or long chain

12   branching are kept to minimum.

13   Among other factors, the present invention is based on our finding that

14   unexpectedly low MVTRs can be achieved from relatively high MWD resins,

15   greater than 4 MWD, wherein the resin is produced from CpCr catalysts as

16   described in more detail below. The resins produced by the process of the

17   present invention have excellent processability while still achieving excellent

18   MVTR properties.

19   <u>BRIEF DESCRIPTION OF THE DRAWINGS</u>

20   Figure 1 is a schematic diagram showing a film of five layers that may be

21   used in an application requiring low moisture vapor transmission rate (low

22   MVTR).

23   Figure 2 is a schematic diagram showing a three-layer film that may be used

24   in an application requiring low moisture vapor transmission rate (low MVTR).

1   DETAILED DESCRIPTION OF THE INVENTION

2   One important aspect of the present invention is the achievement of a process

3   for producing a polyolefin resin which, when formed into a film, has a low

4   MVTR, while also achieving particularly attractive processing characteristics

5   for the resin.

6   MVTR (Moisture Vapor Transmission Rate) or WVTR (Water Vapor

7   Transmission Rate), as it is sometimes called, is determined for a resin in a

8   two-step process (three-step if one includes the pelleting step for the resin

9   fluff from the reactor), involving extrusion and measurement. Resin produced

10   in a slurry or gas phase process is first compounded into pellets which are

11   extruded into film using a blown or cast film extrusion method. Since

12   extrusion conditions have a significant effect on the MVTR exhibited,

13   extrusion temperatures, extruder output rates, cooling rates, film gauge, and,

14   in the case of blown film, blow-up ratio, are controlled during extrusion of the

15   resin and held constant when comparing the MVTR properties of two or more

16   resins.

17   Following the extrusion of the resin into film, the actual measurement of

18   MVTR is performed using a Mocon Permatran-W3/31 MVTR testing system,

19   or equivalent. The Mocon instrument for measuring water permeability was

20   developed by Modern Controls, Inc. To accomplish the MVTR measurement,

21   a 10 x 10 cm sample is cut from a random area of the film. The sample is

22   then mounted in a sample test cell and placed in the Mocon Permatran W3/31

23   unit. In the unit, the test film is exposed to a constant continuous flow of dry

24   nitrogen gas across one side of the film, exhaust side, and a constant

25   continuous flow of controlled humidity nitrogen gas across the other side,

26   carrier side. Water vapor passes from the humidified nitrogen side of the test

27   cell through the film and into the dry nitrogen side of the test cell. A

28   modulated infrared photodetection system on the exhaust side of the test cell

29   measures the variation in the absorption of infrared energy caused by the

1   water vapor which has transmitted through the film. By comparing the

2   amplitude of the output signal obtained from the infrared photodetection

3   system mounted on the test cell with the amplitude of a signal from a

4   reference cell in the same instrument containing a film with a known

5   transmission rate, the transmission rate of the test film is determined.

6   By convention, the value obtained for MVTR is expressed as grams of water

7   transmitted per 100 square inches per one mil (one thousandth of an inch)

8   thickness in a 24-hour period (or, in metric system, grams of water transmitted

9   per square meter per mm thickness in a 24-hour period).

10 The resins produced by the process of the present invention have a relatively

11 high MWD. MWD is the ratio of the weight average molecular weight (M_w) to

12 the number average molecular weight.

13 Preferred means of determining M_n and M_w is by Gel Permeation

14 Chromatography (GPC) which is also commonly known as Size Exclusion

15 Chromatography (SEC). For the purpose of references to M_n and M_w in this

16 application, molecular weight is determined using a Waters 150°C liquid

17 chromatograph, three linear mixed bed chromatographic columns, and hot

18 carrier solvent of 1, 2, 4 trichlorobenzene (TCB) at 150°C temperature. The

19 GPC elution volume is converted to the linear-equivalent polyethylene

20 molecular weight (M) by way of a standard calibration method using a

21 high-density linear polyethylene standard of known M_w, M_n values and a broad

22 molecular weight distribution. Equation (1) below is used to calculate the

23 polymer weight fraction (W) of different molecular weights existed in the GPC

24 effluent as detected by an online differential refractomer signal (RI).

25 Equations (2) and (3) are used to calculate the M_w and M_n values of any

26 unknown sample using the predetermined M values from the GPC calibration

27 curve.

28

1
$$(W)i = \frac{(RI)i}{\sum (RI)i} \tag{1}$$

2

3
$$Mw = \left[\frac{\sum Mi * (W)i}{\sum (W)i} \right] \tag{2}$$

4

5
$$Mn = \left[\frac{\sum (W)i}{\sum (W/M)i} \right] \tag{3}$$

6

7   Another important aspect of the present invention is the catalyst which is used

8   for forming the MVTR resin. As indicated above, the preferred catalyst used

9   in the present invention is a cyclopentadienyl chromium compound on a

10 support.

11 As used herein, the term "cyclopentadienyl" refers to unsubstituted

12 cyclopentadienyl. However, the cyclopentadienyl ring may contain one or

13 more substituents, preferably substituents which do not interfere with the Cr

14 (chromium) compound's ability to function as an alpha-olefin polymerization

15 catalytic site. Examples of substituted cyclopentadienyl include

16 pentamethylcyclopentadienyl, methylcyclopentadienyl,

17 t-butylcyclopentadienyl, and pentaphenylcyclopentadienyl, as well as

18 compounds where the substituent forms a multi-cyclic ring with the

19 cyclopentadienyl ring. Examples of these multi-cyclic rings include indenyl

20 and fluorenyl rings. For the sake of simplicity, the abbreviation "Cp" will be

21 used herein to refer to unsubstituted cyclopentadienyl. However, substituted

22 Cp groups, including indenyl, which in turn may be substituted, are preferred

23 for use in the present invention. Pentamethylcyclopentadienyl is an especially

24 preferred substituted Cp. Indenyl is treated as a substituted Cp for purposes

25 of the present patent application.

26 Preferably, the Cr metal atom in the CpCr compound has an oxidation state of

27 +3 in the catalyst as produced.

1 Preferably, these CpCr compounds have, in addition to one cyclopentadienyl

2 group, at least one hydrocarbyl group bonded to the metal atom. As used

3 herein, the term "hydrocarbyl" refers to alkyl, alkenyl, aryl, aralkyl and alkaryl

4 radicals and the like. Exemplary hydrocarbyl radicals include, but are not

5 limited to, methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, neopentyl,

6 isobutyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, benzyl, and other similar

7 groups. Additionally, organosilyl groups, such as trimethylsilyl methyl, i.e.,

8 $(CH_3)_3SiCH_2-$, and the like can be used. If more than one hydrocarbyl group

9 is bonded to the metal atom, they can be independent or linked, i.e., they can

10 form a 3-, 4-, 5-, 6-, 7-membered metallocycle. Preferably, the hydrocarbyl

11 group is sigma bonded to the Cr metal. Other functional substituents which

12 may be used on the Cp include ER, where E=O, or S; ER_2, where E=B, N, or

13 P; and SiR_3. R is an organic moiety.

14 In addition to the cyclopentadienyl and hydrocarbyl groups, the Cr compounds

15 used in the present invention may also contain one or more sigma donor

16 stabilizing ligands. These ligands contain an atom, such as oxygen, nitrogen,

17 phosphorus or sulfur, which has a non-bonded electron pair. Examples of

18 these ligands include, but are not limited to, ethers, amines, phosphines and

19 thioethers. Ethers such as tetrahydrofuran (THF) and amines such as

20 pyridine are preferred. Compounds with pyridine are most preferred for use in

21 the process of the present invention.

22 Examples of the Cr compounds useful in this invention include, but are not

23 limited to, compounds having the following general formulas:

24 $(C_5(R')_5)_aCrX_bL$ (I)

25 $[(C_5(R')_5)_aCrX_b]_c$ (II) or

26 $[(C_5(R')_5)_aCrX_b(L)_m]+[A]-$ (III)

1   wherein $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring;

2   R' is at each independent occurrence hydrogen, a hydrocarbyl radical having

3   1-20 carbon atoms, or adjacent R' groups may together form one or more

4   rings;

5   X is a hydrocarbyl radical having 1-20 carbon atoms (for example, a

6   monovalent saturated aliphatic or alicyclic radical or a monovalent aromatic

7   radical, or combinations thereof; X, in addition, may be a monovalent

8   hydrocarbyloxy, amido, phosphido or sulfido radical or combinations thereof:

9         $a = 1$ or 2, $b = 1$ or 2 where $a + b = 3$;

10        $c = 1$ or 2 with the proviso that when $c = 2$ then X is alkyl;

11   L is at each independent occurrence a sigma donor stabilizing ligand;

12        $m = 1$ to 2 inclusive; and

13   A is an anion.

14   Examples of compounds having Formula (I) above include, but are not limited

15   to, pentamethyl $CpCr(CH_3)_2(THF)$, pentamethyl $CpCr(Bzyl)_2(THF)$,

16   pentamethyl $CpCr(Bzyl)_2(Pyr)$, pentamethyl $CpCr(CH_3)_2(Pyr)$, pentamethyl

17   $CpCr(TMSM)_2(Pyr)$, pentamethyl $CpCr(TMSM)_2$, pentamethyl

18   $CpCr(CH_3)_2(DMAP)$, pentamethyl $CpCr(CH_3)_2(PMe_2Ph)$, pentamethyl

19   $CpCr(CH_3)_2$(3,5-Lutidine), and pentamethyl $CpCr(CH_3)_2$ (DMAP), where Bzyl

20   is benzyl, Pyr is pyridine, TMSM is trimethylsilylmethyl, DMAP is

21   N,N-dimethylaminopyridine, and PMe_2Ph is dimethylphenylphosphine.

22   Further examples of the Cr compounds preferred for use in the process of this

23   invention include monomeric Cr compounds, dimeric Cr compounds, and

24   cationic Cr compounds. A preferred monomeric Cr compound is pentamethyl

1      $CpCr(Bzyl)_2(THF)$, [pentamethyl $CpCr(CH_3)_2]_2$ is a preferred dimeric

2   compound, and a preferred cationic compound is [pentamethyl

3      $CpCrCH_3(THF)_2]+[BPh_4]-$. Especially preferred compounds are pentamethyl

4      $CpCr(CH_3)_2(Pyr)$, pentamethyl $CpCr(CH_3)_2(3,5-Lutidine)$ and pentamethyl

5      $CpCr(CH_3)_2(PMe_2Ph)$.

6   Several articles, namely, Theopold, *J. Am. Chem. Soc.* (1988) 110, 5902

7   "Cationic Chromium (III) Alkyls as Olefin Polymerization Catalysts", Theopold,

8   *Acc. Chem. Res.* (1990), 23, 263 "Organochromium (III) Chemistry: A

9   Neglected Oxidation State", and Thomas et al., *J. Amer. Chem. Soc.*, 113

10   (1991), p. 893 et seq. (all of which are incorporated herein by reference)

11   describe syntheses useful in making some of the Cr compounds useful in the

12   process of this invention. Similar procedures can be used to make related

13   compounds.

14   In preferred catalyst systems used in the process of the present invention, an

15   organo chromium compound is deposited on an inorganic support. Suitable

16   inorganic metal oxide supports include silica, alumina, silica-alumina mixtures,

17   thoria, zirconia, magnesium oxide and similar oxides. Suitable inorganic

18   metal phosphates include aluminum phosphate, zirconium phosphate,

19   magnesium-containing alumina phosphate and alumina aluminum phosphate.

20   Silicas, aluminum phosphates and alumina aluminum phosphates are

21   preferred. Suitable silica supports include Davison 952, Davison 948,

22   MS 3030 and MS 3050, Crosfield EP-10 and Crosfield EP17MS. Further

23   examples of useful supports are the following: alumina aluminum phosphates

24   with aluminum to phosphorus ratios of about 5:1 to 1:1 as disclosed in U.S.

25   Patents 4,080,311 and 4,219,444; magnesia-alumina-aluminum phosphates

26   as described in U.S. Patent 4,210,560; zinc oxide-cadmium oxide-alumina-

27   aluminum phosphates such as those disclosed in U.S. Patent 4,367,067; and

28   the calcium, barium, and/or strontium oxide-alumina-aluminum phosphates

29   described in U.S. Patents 4,382,877 and 4,382,878. The acidity of these

30   supports can be adjusted by judicious inclusion of basic metals such as alkali

1   and alkaline earth metals (Ca, Be, Mg, K, Li) to counteract excessive acidity.

2   Other useful supports include magnesium halides, particularly magnesium

3   chloride, such as those described in "Transition Metals and Organometallics

4   as Catalysts for Olefin Polymerization" (1988, Springer-Verlag) edited by W.

5   Kaminsky and H. Sinn and "Transition Metal Catalyzed Polymerizations-

6   Ziegler-Natta and Metathesis Polymerizations" (1988, Cambridge University

7   Press) edited by R. Quirk.

8   The supports useful in this invention should have a high surface area. In

9   general, these supports should have characteristics listed in the following

10 table:

Property	Broad Range	Preferred Range	More Preferred Range
Surface area, m^2/g	25-600	100-400	250-350
Pore volume, cm^3/g	0.25-4	0.7-3	1.5-2.0
Mean particle diameter, microns	20-200	25-140	30-70

11

12 Preferably, the pore size distribution is narrow, with a significant percentage of

13 the pores in the range 150-200 Angstroms. It is also desirable that the

14 support be substantially anhydrous before the Cr compound is deposited on it.

15 Thus, it is desirable to calcine the support prior to deposition of the Cr

16 compound.

17 The supported catalysts used in this invention are readily prepared by

18 techniques known in the art. For example, a solution of the Cr compound in

19 aliphatic, aromatic or cycloaliphatic hydrocarbons, or ethers such as diethyl

20 ether or tetrahydrofuran can be stirred with the support until the Cr compound

21 is adsorbed on or reacted with the support. The amount of Cr compound

22 relative to the amount of support will vary considerably depending upon such

1   factors as the particle size of the support, its pore size and surface area, the

2   solubility of the Cr compound in the solvent employed, and the amount of Cr

3   compound which is to be deposited on the support. However, in general, the

4   amount of Cr compound used is adjusted so that the final metal content

5   (calculated as the element), relative to the support, is in the range of from

6   about 0.01 to about 5 weight percent. In most cases, the most desirable level

7   is in the range of about 0.1 to about 1.5 weight percent.

8   The activity of many of the supported Cr compounds used in the process of

9   this invention is significantly increased when they are employed in conjunction

10 with a co-catalyst. The co-catalysts useful in the practice of the present

11 invention are Group 2 and Group 3 metal alkyls. As used herein, the term

12 "Group 2 and Group 3 metal alkyls" refers to compounds containing a metal

13 from Group 2 or Group 3 of the Periodic Table (such as Mg, Zn, B or Al) to

14 which is bonded at least one alkyl group, preferably a C_1 to C_8 alkyl group.

15 Suitable Group 2 and Group 3 metal alkyls include dialkyl magnesium, dialkyl

16 zinc, trialkylboranes, and aluminum alkyls. Suitable aluminum alkyls include

17 trialkylaluminums (such as trimethylaluminum, triethylaluminum,

18 triisobutylaluminum and trioctylaluminum). Trialkylaluminum with alkyl groups

19 of four carbons or greater are preferred. Other aluminum alkyls useful in the

20 practice of the present invention include alkylaluminum alkoxides (such as

21 diethylaluminum ethoxide and ethylaluminum diethoxide), and alkylaluminum

22 halides (such as diethylaluminum chloride, diethylaluminum bromide,

23 diethylaluminum iodide, diethylaluminum fluoride, ethyl aluminum dichloride,

24 ethyl aluminum dibromide, ethyl aluminum diiodide, ethyl aluminum difluoride,

25 and ethyl aluminum sesquichloride).

26 Preferred aluminum alkyls are aluminoxanes, including those represented by

27 the general formula $(R-Al-O)_n$ for the cyclic form and $R(R-Al-O)_nAlR_2$ for the

28 linear form. In these formulas, R is, at each independent occurrence, an alkyl

29 group (such as methyl, butyl, isobutyl and the like) preferably with more than

30 two carbon atoms, more preferably with 4-5 carbon atoms, and n is an

1   integer, preferably from 1 to about 60. Most preferably, R is an isobutyl

2   group. Mixtures of linear and cyclic aluminoxanes may also be used.

3   Examples of aluminoxanes useful in this invention include, but are not limited

4   to, ethyl aluminoxane, isobutyl aluminoxane, and methyl aluminoxane, and

5   mixtures thereof. Aluminoxanes (also known as "alumoxanes") suitable for

6   use in this invention are described in Pasynkiewicz, "Alumoxanes: Synthesis,

7   Structure, Complexes and Reactions," Polyhedron 9, p. 429 (1990), which is

8   incorporated by reference herein in its entirety.

9   The preferred Group 2 and Group 3 metal alkyls are aluminoxanes and the

10   trialkylaluminums.

11   When used, the Group 2 and Group 3 metal alkyls are used in a Group 2 or

12   Group 3 metal alkyl to Cr compound mole ratio of from about 1:1 to about

13   1000:1. The preferred mole ratio is from about 1:1 to about 100:1.

14   The process of the present invention may be carried out in either solution,

15   slurry or gas phase polymerization processes, and preferably is carried out in

16   a slurry or gas phase process. After the catalyst has been formed, the

17   polymerization reaction is conducted by contacting the monomer charge with

18   a catalytic amount of the catalyst at a temperature and at a pressure and

19   ethylene concentration sufficient to initiate the polymerization reaction. As

20   indicated above, preferably substantially linear polyethylene is produced in the

21   present invention. For a slurry process, an organic solvent may be used as a

22   diluent and to facilitate heat transfer. The polymerization reaction is carried

23   out at temperatures of from about 30°C or less up to about 250°C or more,

24   depending on the equipment design and on the operating pressure, and the

25   particular catalyst being used. Preferably, the temperature is from about 60°C

26   to about 125°C, more preferably 60°C to 100°C. The pressure is dependent

27   on ethylene concentration and is sufficient to initiate the polymerization of the

28   monomer charge, and can be from atmospheric up to about 1000 psig, more

29   preferably about 20 to about 800 psig. For a slurry or solution polymerization,

1   the ethylene concentration in the range of 4-20 weight percent of the solvent

2   or diluent phase is preferred.

3   When the catalyst is used in a slurry or solution type process, an inert solvent

4   or diluent medium is used. The solvent or diluent should be one which is inert

5   to all other components and products of the reaction system, and be stable at

6   the reaction conditions being used. It is not necessary, however, that the inert

7   organic solvent medium also serve as a solvent for the polymer produced.

8   The inert organic solvents which may be used include saturated aliphatic

9   hydrocarbons (such as hexane, heptane, pentane, isopentane, isooctane,

10   purified kerosene and the like), saturated cycloaliphatic hydrocarbons (such

11   as cyclohexane, cyclopentane, dimethylcyclopentane, methylcyclopentane

12   and the like), aromatic hydrocarbons (such as benzene, toluene, xylene and

13   the like), and chlorinated hydrocarbons (such as chlorobenzene,

14   tetracholoethylene, o-dichlorobenzene and the like). Particularly preferred

15   solvents or diluents are isobutane, cyclohexane, hexane and heptane.

16   When the catalyst is used in a gas phase process, preferably it is suspended

17   in a fluidized bed with, e.g., ethylene. Temperature, pressure and ethylene

18   flow rates are adjusted to maintain acceptable fluidization of the catalyst

19   particles and resultant polymer particles. Further descriptions of such a

20   fluidized bed may be found in British Patent 1,253,063, to Karapinka, which is

21   incorporated by reference herein.

22   The resin produced by the process of the present invention is used to produce

23   a film. Referring now to Figures 1 and 2, two alternate preferred product

24   MVTR film constructions are shown. Figure 1 is a five-layer coextruded

25   MVTR film construction. Figure 2 is a three-layer coextruded MVTR film.

26   Known means may be used for coextruding resin to form the respective layers

27   of the coextruded MVTR film illustrated in Figures 1 and 2. Also, the resin

28   produced in accordance with the process of the present invention may be

29   used in a monolayer.

1   One advantage we have found for the resins produced in accordance with the

2   present invention is that they may be advantageously used to form film of low

3   MVTR. Further, the resins produced in accordance with the present invention

4   are advantageous in that the same resin may be used for the skin layer of the

5   coextruded construction and the core layer(s). In typical prior art, a higher

6   (2 g/10 min or higher) melt index HDPE resin is used in the skin layer of the

7   construction and a lower (less than 1.5 g/10 min) melt index HDPE resin is

8   used in the core layer(s) in order to achieve lower MVTR than a film using the

9   lower MI in both the skin and core layers.

10   Referring now to Figures 1 and 2, two alternate preferred product MVTR film

11   constructions are shown. Figure 1 is a five-layer coextruded MVTR film

12   construction. Figure 2 is a three-layer coextruded MVTR film. Known means

13   may be used for coextruding resin to form the respective layers of the

14   coextruded MVTR film illustrated in Figures 1 and 2. Also, the resin produced

15   in accordance with the process of the present invention may be used in a

16   monolayer film. However, commercially viability of monolayer applications is

17   generally dependent on heat sealing qualities of HDPE. Applications of the

18   resin produced by the present invention can be made to produce a monolayer

19   film for barrier properties which when laminated to other films or paper to

20   make a finished product, such as a packaging product.

21

22   One advantage we have found for the resins produced in accordance with the

23   present invention is that they may be advantageously used to form film of low

24   MVTR. Further, the resins produced in accordance with the present invention

25   are advantageous in that the same resin may be used for the skin layer of the

26   coextruded construction and the core layer(s). In typical prior art, a higher

27   (2 g/10 min or higher) melt index HDPE resin is used in the skin layer of the

28   construction and a lower (less than 1.5 g/10 min) melt index HDPE resin is

29   used in the core layer(s) in order to achieve lower MVTR than a film using the

30   lower MI in both the skin and core layers.

31

1   Figure 1 illustrates a preferred five-layer construction. The outer layer or

2   outside skin of the film is layer 1. The core layers are layers 2, 3 and 4. The

3   inside layer, which is referred to as the seal layer, and may come into contact

4   with foodstuffs, is layer 5. Preferably, layer 1 is 10% to 20% of the total

5   thickness, layers 2, 3 and 4 preferably are 60% to 80% of the thickness, and

6   layer 5 is 10% to 20% of the thickness of the product film.

7

8   As referenced in the August 1999 issue of *Plastics Technology* in the article

9   "Keep It Dry" and from common knowledge in the MVTR film market, in the

10   five-layer construction, Layer 1, the skin layer or outside layer of the film is

11   generally a HDPE having a melt index of between 2 and 6 g/10 min. The

12   three core layers, Layers 2, 3 and 4 in the figure, generally consist of a HDPE

13   having a melt index between about 0.5 and 1.5, preferably approximately

14   1.0 g/10 min. The core layers can be fed by three separate extruders or may

15   be formed by splitting the stream from one extruder into two or three

16   independent layers prior to or inside the die. As mentioned above, layer 5 in

17   Figure 1 is the seal layer in the coextruded construction. The seal layer may

18   consist of a single resin, such as a high ethylene vinyl acetate copolymer or

19   may be a blend of several resins. Resins used in the seal layer generally

20   demonstrate a low crystallinity and as such do not appreciably contribute to

21   the MVTR performance of the film.

22

23   Figure 2 illustrates an alternate preferred construction, which is three layers.

24   The outer layer or outside skin of the film in Figure 2 is layer a. The core layer

25   is layer b. The inside layer, which is referred to as the seal layer, and may

26   come in contact with foodstuffs, is layer c. Preferably, layer a is 10% to 20%

27   of the total thickness, layer b preferably is 60% to 80% of the thickness, and

28   layer c is 10% to 20% of the thickness of the product film.

29

30   As is the case in the five-layer construction, the three-layer construction

31   generally utilizes a 2 to 6 g/10 min. melt index HDPE, layer a in Figure 2, in

32   the skin layer. The core layer in the three-layer construction, layer b, is a

1   HDPE generally having a melt index of about 0.5 to 1.5, preferably about

2   1.0 g/10 min. The seal layer, layer c, in the three-layer construction generally

3   utilizes the same type of resins and resin blends commonly found in the

4   five-layer construction.

5

6   An unexpected advantage we have found for the resins produced by the

7   present invention is that the same grade HDPE may be used for both layer a

8   and layer b in the three-layer construction and in layers 1, 2, 3 and 4 and

9   achieve substantially equivalent barrier properties to the conventional systems

10   requiring different grades of HDPE in the skin and core layer(s). Using the

11   same grade HDPE is attractive for film manufacturers for convenience in both

12   production of film and the inventory of resin. Since a HDPE resin produced by

13   the present invention eliminates the need for a separate skin and core layer

14   HDPE resin, film processors can reduce the number of HDPE resins they

15   must inventory and the need for tracking two different HDPE resins within the

16   transfer systems of the plant is eliminated.

17

18   We have found that, using the resin produced in accordance with the present

19   invention, the high MI outside skin (layer a in the three-layer coextrusion and

20   layer 1 in the five-layer coextrusion) of 2 MI or greater per the prior art can be

21   replaced by an approximately 1 MI HDPE resin produced in accordance with

22   the present invention. And, the same 1 MI resin can be used for the core

23   layers, and yet still achieve attractive performance, such as low MVTR for the

24   overall film.

25   The following examples are intended to further illustrate the present invention.

EXAMPLES

Example 1

1

2

3 A preferred catalyst for use in the process of the present invention is prepared

4 as follows: The pentamethyl $CpCr(CH_3)_2(Pyr)$ was prepared following the

5 general description contained in Noh, S.K.; Sendlinger, S.C.; Janiak, C.;

6 Theopold, K. H., *J. Am. Chem. Soc.* (1989), 111, 9127. Lithium

7 cyclopentadienide (0.380 g, 2.67 mmol) was added slowly to a slurry of 1.00 g

8 (2.67 mmol) of $CrCl_3(THF)_3$ in 50 mL of THF. The resulting blue solution was

9 stirred for 2 hours. Pyridine (0.222 g, 2.80 mmol) was added resulting in the

10 deposition of a light blue solid. Stirring was continued for 1 hour after which

11 was added (dropwise) 2.0 equivalents (3.80 mL of 1.4M solution in Et_2O) of

12 methyllithium. The dark green-brown solution was stirred an additional 0.5 hr.

13 and then taken to dryness under vacuum. The dark solid was extracted into

14 pentane, filtered to remove metal halides, and taken dryness. The remaining

15 solid was re-extracted into pentane, filtered, and the solvent was reduced until

16 microcrystals appeared. The dark brown solution was kept at -40°C overnight

17 resulting in the deposition of black crystals. The crystals were collected and

18 dried under vacuum. Silica (Davison 948) activated at 700°C, 300 g was

19 charged to a flask and 1600 ml heptane was added in an inert atmosphere.

20 The contents are heated to 70°C with mechanical stirring to form a silica

21 slurry.

22 Then 15 g of the pentamethyl $CpCr(CH_3)_2(Pyr)$ was added in 2-3 g aliquots to

23 the silica slurry over the course of 1 hour. The contents of the flask was

24 stirred for 12 hrs. at 70°C. The contents of the flask were cooled to room

25 temperature and filtered with a fritted glass filter. The solid was dried on the

26 filter under vacuum at 40-45°C for 4 hrs. and further dried an additional

27 10-12 hrs. by passing argon up through the fritted filter at 40-45°C. The solid

28 catalyst was then transferred to a receiving vessel.

1   Example 2

2   Gas Phase

3   Supported CpCr catalyst, as described in Example 1, was introduced

4   continuously into a 24-inch outside diameter gas phase fluid bed

5   polymerization reactor to polymerize ethylene. Isobutyl aluminoxane (IBAO)

6   was fed to the reactor as a co-catalyst at various Al:Cr ratios including at an

7   atomic ratio of (Al/Cr) of eight. Hydrogen was fed to the reactor to assist in

8   control of the molecular weight of the polyethylene product. The reactor

9   operating conditions were:

Polymerization Temperature	210°F
Polymerization Pressure	300 psig
Ethylene Pressure	260 psi
Gas Phase $H_2/C_2^=$ Molar Ratio	0.025
IBAO Feed Al/Cr Molar Ratio	8
Production Rate PE	22 lbs/hr

16   The resulting polyethylene product had a density of 0.9640 g/cc, a MI of

17   0.67 g/10 min, and a melt flow ratio (MFR) of 109.

18   We have found that resins with low MVTR are produced in accordance with

19   the present invention using gas phase; however, slurry (liquid) phase reaction

20   conditions are preferred as described in the next example.

21   Example 3

22   Slurry Polymerization

23   Slurry polymerization of ethylene in isobutane was carried out in a high

24   pressure pilot plant equipped with a 50-gal loop reactor operated in a

25   continuous mode at a pressure of 600 psig and temperature of 180°F to

1   200°F. Operating conditions and product properties are described further

2   below and summarized in Tables A and B below.

3   The catalyst as prepared in Example 1 was continuously injected as an

4   isobutane slurry to the bottom of the loop. The co-catalyst,

5   isobutylalumoxane, IBAO, was continuously metered as a 0.8 wt. % solution

6   in hexane or isopentane at a rate of 100 to 300 cc/hr into the catalyst feed line

7   to provide a 15 to 45 seconds pre-contact and reaction time prior to flowing

8   into the loop reactor.

9   Ethylene and hydrogen were continuously metered into an isobutane feed at

10 the top of the loop. An additional isobutane feed stream was maintained

11 across the face of the circulating pump.

12 The reaction slurry was circulated at a rate of 2300 gal/min via a Sultzer

13 Bingham circulating pump. Slurry was discharged from the loop via a letdown

14 valve operated by pressure control, 585 to 600 psi differential.

15 The slurry leaving the loop passed into a flash stage for primary removal of

16 isobutane, ethylene, and hydrogen and into a rotary drier stage for final

17 degassing and transport into collection drums. Gas from the flash stage was

18 continuously analyzed for its makeup. The solid catalyst injection quantity

19 was adjusted to control the desired ethylene content in the reactor at 4 to

20 10 wt. % based on a constant quantity of ethylene and isobutane feed and to

21 maintain a constant production rate of polyethylene. Polyethylene molecular

22 weight was controlled by the hydrogen concentration in the isobutane. The

23 hydrogen feed was adjusted to maintain a constant ratio of hydrogen to

24 ethylene in the reactor, as measured by the gas composition in the flash tank.

25 The polymerization product, the polyethylene fluff, was chemically

26 characterized according to the following methods.

1   The Melt Index was used as a measure of molecule weight and MFR was

2   used as a measure of MWD. MFR was measured according to

3   ASTM 1238-90b as a function of MI and a HLMI. MFR is the ratio of HLMI to

4   MI. HLMI and MI are determined in accordance with the currently approved

5   ASTM method.

6   The density of the fluff and pellets was determined in accordance with

7   ASTM 1928-90. GPC was used for both fluff and pellets to measure

8   molecular weights as M_w, M_n, and MWD. Melting points were determined by

9   DSC according to ASTM E 794.

10   The polyethylene fluff was compounded with an antioxidant, Irganox

11   (registered trademark of Ciba-Geigy) B9355FF, at a level of 400 to 880 ppm

12   weight, into pellets on a Werner Pfleiderer 30 mm twin screw extruder. The

13   typical conditions for pelletization include oxygen exclusion via a nitrogen

14   purge, 55 lbs/hr rate, 200 rpm screw speed; temperature (°F) profile over

15   zones 1-6 at 200, 300, 350, 400, 450. The water bath was maintained at near

16   ambient conditions. The pellets were formed into film and the film samples

17   tested according to ASTM F 1249, for MVTR, as reported in Table B.

Table A

Operating Conditions and Resin Properties

Run #	Temp °F	iC$_4$ lbs/hr	C$_2$ lbs/hr	IBAO cc/hr	C$_2$ wt. %	H$_2$/C$_2$ mol%/wt. %	Cat Base/Cr, wt. %	MI	MFR	PE, rate lbs/hr
1	190	65	30	600	8.0	0.0020	MS3030/1.0	1.1	53	25
2	185	65	30	300	9.0	0.0019	DAV948/0.8	1.1	45	25
3	205	65	30	300	8.0	0.0019	DAV948/0.8	1.0	57	
4	190	65	30	300	8.4	0.0019	DAV948/0.8	1.0	50	

Table B

Resin, Pellet and Film Data

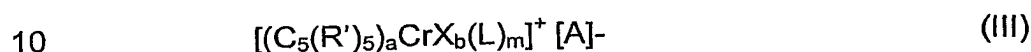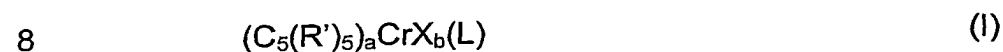| Run #	Mn	Mw	MWD	P g/cc	Cr/Al ppm/ppm	MVTR	FTIR Methy/Vinyl	MVTR % Control
1	21,500	123,000	5.7	0.963	0.8/13	0.226		17.8
2	23,800	120,000	5.0	0.962	<0.1/12	0.249	21	8.5
3	18,800	132,000	7.0	0.962	1.4/10	0.236		15.2
4	21,900	120,600	5.5	0.963	0.4/12	0.258	17.8	15.5

1 WHAT IS CLAIMED IS:

2 1. A process for making an ethylene homopolymer having a polydispersity
3   above 4, and wherein the homopolymer is suitable for producing a film
4   having an MVTR below 0.4, which comprises contacting ethylene with a
5   catalyst comprising a cyclopentadienyl chromium hydrocarbyl compound
6   on a solid support, under slurry or gas phase polymerization conditions.

7 2. A process in accordance with Claim 1 wherein the film has an MVTR
8   below 0.3.

9 3. A process in accordance with Claim 1 wherein the film has an MVTR
10   below 0.25.

11 4. A process in accordance with Claim 1 wherein the polydispersity is
12   above 6.

13 5. A process in accordance with Claim 1 wherein the polydispersity is
14   above 7.

15 6. A process in accordance with Claim 1 wherein the CpCr compound is in
16   cationic form.

17 7. A process in accordance with Claim 1 wherein the chromium is in an
18   oxidation state of +3.

19 8. A process in accordance with Claim 1 wherein the catalyst includes a
20   co-catalyst comprising an aluminoxane.

21 9. A process in accordance with Claim 8 wherein the co-catalyst comprises
22   isobutyl aluminoxane.

1   10.   A process in accordance with Claim 1 wherein the support comprises
2   silica and the weight percent chromium on the silica is between 0.5 and
3   1.5.

4   11.   A process in accordance with Claim 1 wherein the polymerization is
5   carried out under slurry conditions.

6   12.   A process in accordance with Claim 1 wherein the chromium compound
7   has the formula:

8                    $(C_5(R')_5)_aCrX_b(L)$ (I)

9                    $[(C_5(R')_5)_aCrX_b]_c$ (II) or

10                   $[(C_5(R')_5)_aCrX_b(L)_m]^+ [A]-$ (III)

11   wherein $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl
12   ring;

13   R' is at each independent occurrence hydrogen, a hydrocarbyl radical
14   having 1-20 carbon atoms, or adjacent R' groups may together form one
15   or more rings;

16   X is a hydrocarbyl radical having 1-20 carbon atoms;

17   a=1 or 2, b=1 or 2 where a+b=3;

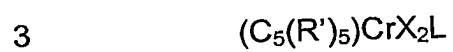18   c=1 or 2 with the proviso that when c=2 then X is alkyl;

19   L is at each independent occurrence a sigma donor stabilizing ligand;

20   m=1 to 2 inclusive; and

21   A is an anion.

1   13.   A process in accordance with Claim 12 wherein the chromium

2   compound has the formula:

3           $(C_5(R')_5)CrX_2L$

4   14.   A process in accordance with Claim 13 wherein $(C_5(R')_5)$ is
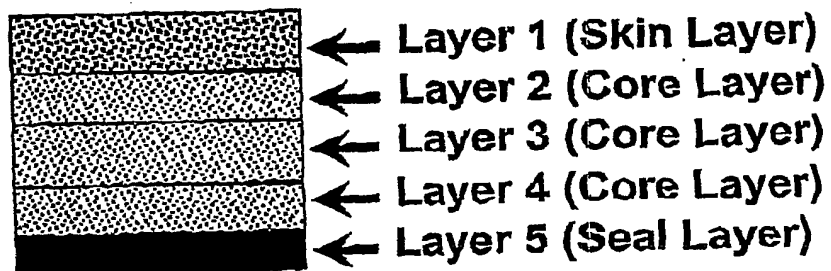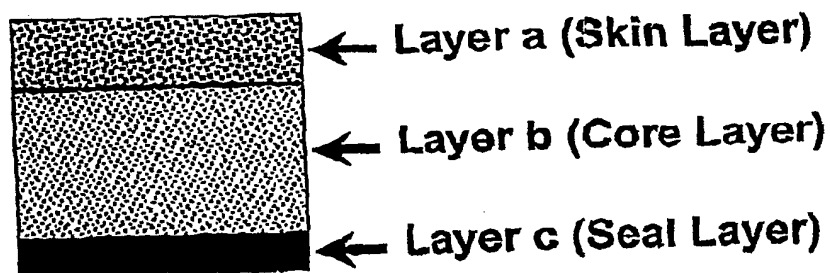
5   pentamethylcyclopentadienyl.

Figure 1

Layer 1 (Skin Layer)
Layer 2 (Core Layer)
Layer 3 (Core Layer)
Layer 4 (Core Layer)
Layer 5 (Seal Layer)

Figure 2

Layer a (Skin Layer)

Layer b (Core Layer)

Layer c (Seal Layer)

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) :C08F 4/02, 4/69, 4/78
US CL :526/129, 160, 169, 352
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : 526/129, 160, 169, 352
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST, WEST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,169,817 A (DAWKINS et al) 08 December 1992, Examples 1-10.	1-5, 11
X	US 5,418,200 A (CARNEY et al) 23 May 1995, Examples 1-25.	1-14

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
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"O" document referring to an oral disclosure, use, exhibition or other means	
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Date of the actual completion of the international search	Date of mailing of the international search report
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